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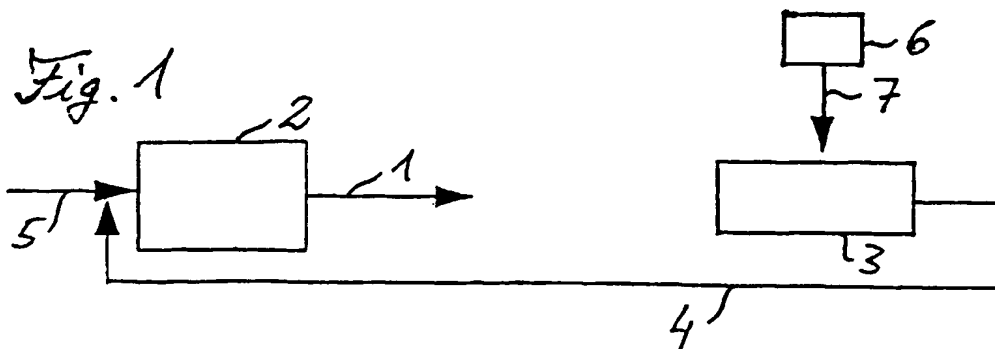
(54) Exhaust gas purifying system with nitrogen oxide adsorber and operation method therefor

(57) The invention is related to an exhaust gas purifying system having a nitrogen oxide adsorber together with a means of alternatively operating the same in adsorption and desorption mode and for passing the exhaust gas of a combustion source through the same at least in adsorption mode, said means including a desorption gas supply unit for supplying a desorption gas to the adsorber in desorption mode, as well as to a method of operating such system.

According to the invention the desorption gas supply unit includes means for accomplishing a swing of the

nitrogen oxide partial pressure when switching to desorption mode, preferably by supplying a water-containing, wet desorption gas during desorption mode, while the adsorber temperature may be increased or decreased or kept constant. With these means said adsorber can be effectively regenerated according to the operation method of the present invention.

The invention can be used for example in motor vehicles.



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Description

[0001] The invention relates to an exhaust gas purifying system according to the precharacterizing part of claim 1 and to a method of operating an exhaust gas purifying system according to the precharacterizing part of claim 7.

[0002] Such systems and methods are e.g. conventionally used for purifying the exhaust gases from combustion engines of motor vehicles. The nitrogen oxides being produced in higher quantities particularly during lean-burn operation of the motor, are temporarily stored in the adsorber by adsorption, and are released again at an appropriate time during the desorption operation of the system. The released nitrogen oxides are then properly converted, e.g. by exhaust gas recirculation or adding a reducing agent, like ammonium or urea or an exhaust gas stream of rich composition, i.e. having a more than stoichiometric fuel amount. Such a rich exhaust gas stream can be provided e.g. by switching the motor operation to rich-burn operation mode by post-injection of fuel into the motor combustion chamber or by additional fuel injection into the exhaust manifold.

[0003] In patent publication DE 43 19 294 C1 exhaust gas purifying systems and methods of operation of this type are described, in which two catalytic adsorbers in parallel conduit branches are alternately operated in adsorption and desorption mode or in which, when only one catalytic adsorber is present, a bypass conduit is provided through which during the desorption mode at least a main part of the exhaust bypasses the catalytic adsorber and is passed through the three-way catalytic converter. A Perovskite material, in particular LaCoO_3 , is mentioned as the adsorber material. To carry out the desorption operation, the catalytic adsorber is heated to a desorption temperature higher than its operation temperature during adsorption mode, to which aim an electric heating device is provided. In addition, the supply of an air stream or a portion of the exhaust gases emitted from the motor as a purging air stream can be provided to expel the desorbed nitrogen oxides off the catalytic adsorber and supply them to an exhaust gas recirculation pipe. The air stream may be heated by the heating device before or at entering the catalytic adsorber.

[0004] It is the technical problem of the invention to provide for an exhaust gas purifying system and an operation method therefor as mentioned above, which are able to accomplish with relatively low effort an effective adsorption of nitrogen oxides included in the exhaust gas as well as an effective desorption thereof and thus an effective regeneration of the adsorber.

[0005] The invention solves this problem by providing an exhaust gas purifying system having the features of claim 1 as well as of a method having the features of claim 7.

[0006] The exhaust gas purifying system of claim 1

characteristically includes means for accomplishing a swing in the nitrogen oxide partial pressure when switching from adsorption to desorption mode. It turns out that such pressing swing can significantly improve the desorption capability, in particular for appropriate adsorption materials and in special cases even without increasing the temperature.

[0007] Preferably, the pressure swing means comprise means for supplying to the adsorber a water-containing, wet desorption gas during desorption operation, as stated in claim 2. It turns out that the use of wet, instead of dry, desorption gas can lead to an improved desorption capability when maintaining the other process parameters constant. In particular, an air stream wetted with water can be used.

[0008] It is assumed that the desorption-assisting behaviour results from the water involved as well as from the fact that the supply of a desorption gas changes the nitrogen oxide partial pressure in the adsorber when switching from adsorption to desorption mode. Both effects can have an influence on the reaction equilibrium equations and can in this way favor the desorption.

[0009] A preferred embodiment of the exhaust gas purifying system as given in claim 3 includes means for maintaining, increasing, or even reducing the temperature in the adsorber during the desorption mode, as compared with the temperature during adsorption mode. Using the temperature reducing means makes it possible to maintain the adsorber during desorption at a temperature lower than that during adsorption mode. Here, it turns out surprisingly, and in contrast to the usual increase in temperature during desorption, that by combining such a temperature decrease with the supply of the water containing wet desorption gas, an effective desorption can be obtained. In particular, the temperature reducing means can consist of means which supply the water-containing, wet desorption gas at a temperature lower than that of the adsorption operation temperature of the adsorber, e.g. at room temperature, so that the cool desorption gas is able to cool the adsorber as desired and with low effort.

[0010] In a further preferred system as given by claim 4 a catalytic converter with an oxidizing function, e.g. a pure oxidation catalytic converter or a three-way catalytic converter, precedes the nitrogen oxide adsorber. In adsorption mode the exhaust gas output from the exhaust gas catalytic converter is fed to the adsorber, while this exhaust gas link is closed during the period of the corresponding desorption phase, the exhaust gas output from the oxidizing catalytic converter being passed, for example, through another adsorber which at the same time is in adsorption mode. In a further preferred embodiment an oxidizing function is combined with the adsorbent material, e.g. by dispersing a noble metal such as platinum on the adsorbent solid. This oxidation function fulfills the role of the oxidation catalytic converter placed in front of the

absorbent explained in the previous embodiment.

[0011] In a further preferred embodiment of the exhaust gas purifying system as claimed in claim 5 there are provided a desorption gas supply unit such that during desorption mode an exhaust gas from a lean-controlled combustion process not passed through an oxidizing catalytic converter before may be supplied to the adsorber, as well as means for increasing the temperature in the adsorber during desorption mode. It turns out that by choosing appropriate adsorber materials an effective desorption can be accomplished by supplying the exhaust gas stream to the adsorber and increasing the temperature in the adsorber as compared to that during adsorption mode.

[0012] In a preferred embodiment of the exhaust gas purifying system as given by claim 6 the adsorber includes a special material, namely a Na-Y, Ba-Y or Ba-La(x%) \cdot Y zeolite material, with $0 < x < 100$, or a heteropol-yacid material of the formula

$H_3NM_{12}O_{40} \cdot 6H_2O$ or $H_4NM_{12}O_{40} \cdot nH_2O$ (with $M = W$ or Mo and $N = P, Si, \text{ or } Ge$, and n an integer, e.g. $n = 14, 15, \text{ or } 24$). It turns out that adsorbers with these adsorber materials have a sufficient adsorption capability and can be effectively regenerated by supplying the water-containing, wet desorption gas, and that can be achieved even at the same temperature as for the adsorption phase.

[0013] The operation method according to claim 7 characteristically includes to induce a nitrogen oxide partial pressure swing when switching from adsorption to desorption mode, preferably by the supply of a water-containing, wet desorption gas to the nitrogen oxide adsorber during desorption mode as claimed in claim 8. This method is in particular suited for the operation of the exhaust gas purifying system of any one of claims 1 to 6. As stated above, a use of such wet instead of a dry desorption gas can promote the desorption.

[0014] In a preferred embodiment as given by claim 9 the method includes selection of a desorption temperature in the adsorber lower than that during adsorption. This is in contrast to the usual temperature increase during desorption mode. Surprisingly it turns out that in particular also with this temperature decrease in connection with using the water-containing, wet desorption gas a sufficient desorption can be obtained. In a preferred embodiment of the method as given by claim 10 this temperature reduction for the desorption can be obtained with particularly low effort by supplying the wet desorption gas with a temperature lower than the adsorption operation temperature.

[0015] In a preferred embodiment of the method as given by claim 11 the desorption temperature is chosen to be lower than 200°C and preferably lower than 100°C . The methods according to claims 7 to 9 are particularly suited for operation of the system according to claim 3.

[0016] Within the operation method according to claim 12, characteristically a temperature increase as

compared with the adsorption operation is provided in connection with the supply of a special desorption gas, namely a water-containing, wet desorption gas or an exhaust gas stream resulting from a lean-controlled combustion process, for the purpose of regeneration of a nitrogen oxide adsorber, the adsorber material of which being appropriately selected from a group of suited materials. It turns out that also by such desorption process control a satisfactory desorption is obtained.

[0017] Preferred embodiments of the invention are illustrated in the drawings described below with reference thereto, in which drawings

Fig. 1 shows a block diagram of the part of interest herein of an exhaust gas purifying system having an adsorber being in desorption mode with isothermal desorption gas supply,

Fig. 2 shows a block diagram corresponding to figure 1, but for a modified exhaust gas purifying system with heating desorption gas supply,

Fig. 3 shows a block diagram corresponding to figure 1, but for a modified exhaust gas purifying system with cooling desorption gas supply, and

Fig. 4 shows a plot diagram to illustrate an adsorption and desorption cycle of a system according to figure 3.

[0018] In figures 1 to 3 only the part of interest herein of a respective exhaust gas purifying system is shown, which system is used to purify the exhaust gases 1 of an internal combustion engine 2 being e.g. generated by a motor vehicle. In all three cases the exhaust gas purifying system comprises a nitrogen oxide adsorber 3 and an exhaust gas recirculation 4. In the illustrated desorption mode, the gas emanating from the nitrogen oxide adsorber 3 and including the desorbed nitrogen oxides is recirculated through the exhaust gas return conduit 4 into an intake manifold 5 of the motor 2.

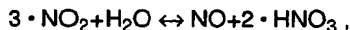
[0019] In adsorption mode of the adsorber 3 the exhaust gas 1 emitted from the motor 2 preferably driven in lean operation is passed through the adsorber 3 which adsorbes the nitrogen oxides contained in the exhaust gas. Here it is preferred to position an oxidizing catalytic converter, not shown, in front of the adsorber 3, which oxidizing catalytic converter besides other functions accomplishes an at least partial oxidation of NO to NO_2 . The adsorber material for the adsorber 3 is in this case suitably chosen such that a co-adsorption of NO as well as NO_2 is achieved. In desorption mode the exhaust gas supply from the oxidizing catalytic converter to the adsorber 3 is stopped, as indicated in fig-

ures 1 to 3 by the missing link of the exhaust gases 1 output from the motor 2 to the adsorber 3.

[0020] Further, the exhaust gas purifying system contains other exhaust manifold components of known type, which need not be mentioned in detail here. For example, a multiplicity of parallel adsorbers and/or a bypass conduit for the adsorber 3 could be provided analogous to the exhaust manifold realizations disclosed in the above-cited DE 43 19 294 C1.

[0021] The present inventive exhaust gas purifying system and the corresponding inventive operation method for such system are characterized by the selection of special desorption measures in connection with using proper adsorber materials. This is based on the following findings.

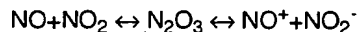
[0022] When using a Na-Y zeolite material as adsorber material for a standard lean-burn diesel motor exhaust gas, this material shows a high and reversible nitrogen oxide adsorption capacity at temperatures below 200°C. However, it is found that in this case substantially only NO₂ is adsorbed, while NO is even produced additionally in small quantities. This material also shows sulfur poisoning effects, because it irreversibly adsorbs SO₂ contained in the exhaust gas at the sites which are otherwise responsible for the reversible adsorption of NO₂. Investigations reveal the adsorbed NO_x species to be nitrate-like. Heating is required to desorb and decompose the same. Experiments have further shown that water contained in the exhaust gas influences the adsorption and desorption process. Under the process conditions mentioned above, based on these investigations the following reaction equilibrium upon contacting the Na-Y zeolite material with oxidized exhaust gas can be proposed:



wherein the nitric acid yields the nitrate species on the basic zeolite material.

[0023] A complete different behaviour is observed when the same Na-Y zeolite material is calcined at 600°C in dry air and then used as an adsorber material for a lean exhaust gas, i.e. one emanating from a lean-burn operation of the corresponding combustion source, at a temperature between 200°C and 350°C. In this case a co-adsorption of NO and NO₂ is observed. By altering the NO/NO₂ ratio of the exhaust gas, it is shown that NO is adsorbed only in the presence of NO₂. Further, it is found that the nitrogen oxide adsorption capacity, when SO₂ is present in the exhaust gas, does not decrease, since the adsorption of SO₂ is strongly temperature dependent. While a significant SO₂ adsorption takes place at 150°C, no SO₂ adsorption is observed at 250°C. The nature of the adsorbed NO_x species is also temperature dependent, nitrite species being found on the adsorber material after adsorption of a mixture of NO and NO₂. With these observations several adsorption equilibrium reactions, described in the

literature for zeolites at low temperatures using dry gases or for the formation of nitrous acid, fit as follows:



and



[0024] The nitrous acid yields the nitrite species on the active adsorption sites of the zeolite material.

[0025] Further investigations in this direction have now shown that said Na-Y adsorber material can be regenerated quite easily by a change or swing of the NO_x partial pressure and/or the temperature, wherein some different procedures turn out to be particularly suited, as described below in more detail with reference to the systems shown in figures 1 to 3. The adsorption operation in these systems with Na-Y adsorber material in the adsorber 3 is carried out in the temperature region of co-adsorption of NO and NO₂ between about 200°C and about 350°C.

[0026] In figure 1 a first method of this kind is illustrated, in which for example a Na-Y zeolite material pre-treated at 600°C by calcination is used as adsorber material in the adsorber 3, which material initially shows an adsorption capacity of about 8mg NO per gram adsorber material. We use the convention here, and in the following, that all the nitrogen oxide (NO_x) molecules are counted as NO when specifying adsorption capacity. This enables comparisons to be made more easily when mixed NO-NO₂ adsorptions are measured. Adsorber operation means are provided in the system of figure 1 to carry out the desorption cycles, which means include a desorption gas supply unit 6 able to prepare a watercontaining, wet air stream 7 and to supply the same substantially isothermally into the adsorber 3, i.e. the wet air stream 7 is heated to the operation temperature of the adsorber 3 by a corresponding heater before entering the adsorber 3. After several alternating adsorption and desorption cycles a steady adsorption and desorption capacity of about 2,8mg NO per gram adsorber material results under these conditions.

[0027] In an alternative method, as illustrated with respect to the system of figure 2, the same Na-Y zeolite material is used, and the adsorption-desorption cycles run like the ones in the system of figure 1 except that in desorption mode the adsorber material is heated above the operation temperature in adsorption mode by supply of heat Q. This heat supply is done preferably through the wet air stream 7a which is supplied to the adsorber 3 during the desorption, i.e. the adsorber operation means in this case comprise a desorption gas supply unit 6a which heats the wetted air stream by a corresponding heater to the desired temperature higher than the adsorption operation temperature of the adsorber 3 and supplies the provided hot, wet air stream 7a to the

adsorber 3. In doing so the adsorber 3 is heated from the adsorber temperature range between 200°C and 350°C through a significantly higher temperature of typically up to about 500°C. In addition to the desorption portion effected by the supply of wet air and the NO_x partial pressure swing caused therefrom, when reaching the increased temperature a second desorption portion appears caused by the temperature increase, resulting in a practically complete regeneration of the adsorber material so that its initial, high NO_x adsorption capacity of about 8mg NO per gram zeolite material can be maintained.

[0028] In a modification of the method described with respect to figure 2, a non-oxidized, hot exhaust gas stream can be supplied to the adsorber 3 for desorption purposes instead of the hot, wet air stream 7a. In particular, the exhaust gas 1 directly output from motor 2 can be used in this respect, with bypassing an eventually interposed oxidizing catalytic converter, especially when motor 2 is a diesel motor and is operated lean. Experiments have shown that also with such exhaust desorption gas stream a practically complete regeneration of the adsorber 3 can be accomplished when raising the desorption temperature to at least about 400°C.

[0029] Another approach according to the present invention, specifically regarding the desorption cycles, is illustrated with reference to the system of figure 3. In this method the adsorber operation means include a desorption gas supply unit 6b which prepares a wet air stream 7b as a desorption gas stream and supplies the same to the adsorber 3 at a temperature lower than the adsorption operation temperature. In particular it is possible to supply the wet air stream to the adsorber 3 at room temperature. In this way a temperature decrease takes place when switching from adsorption to desorption mode in addition to the NO_x partial pressure swing caused by the supply of the wet air stream. This adsorber cooling to a temperature lower than 200°C, preferably to a temperature in the range of 100°C or less, surprisingly also results in a satisfactory regeneration of the adsorber material. Laboratory experiments show, for example, that in wet air atmosphere at 100°C more nitrogen oxides are released than at 250°C and that the desorption depends on the water content of the desorption gas. In dry air no NO_x desorption is observed under the given conditions. Experiments show, however, that a water content between about 1% and about 10% together with a temperature decrease can already lead to a practically complete desorption. The method as explained with respect to the system of figure 3 has the great advantage that no heating of the adsorber 3 or the desorption gas stream supplied thereto is required, but the latter can be supplied to the adsorber 3 at room temperature and removes heat Q therefrom, so that the desired temperature decrease is accomplished. Separate cooling means are thus not necessary for this purpose. With this regeneration method a steady NO_x adsorption capacity of more than

7mg NO per gram zeolite material has been reached.

[0030] The Na-Y zeolite material is found to be a suitable adsorber material for all desorption methods explained above, which material allows for a co-adsorption of NO and NO₂ in a favorable temperature range between 200°C and 350°C without sulfur poisoning problems in absorption mode and also allows for a substantially complete regeneration of the adsorber 3 in desorption mode. The Na-Y zeolite material can be used in powder form or in the form of a monolithic adsorber.

[0031] Instead of the Na-Y zeolite material, alternative adsorber materials can be used, while maintaining the advantages of the operational method of the present invention as described, such as a Ba-Y zeolite material or a Ba-La(x%)-Y zeolite material, the latter being a Ba-Y zeolite material with an admixture of x%La, with 0 < x < 100. These zeolite materials show a high adsorption capacity for NO₂ in the temperature range between 80°C and 300°C, the adsorption mechanism being similar to the one described above for the adsorption by a Na-Y zeolite material below 200°C. Preliminary investigations show that to regenerate these zeolite materials preferably a temperature increase above the temperature level of the absorption mode should be chosen, which temperature increase depends on the composition of the supplied desorption gases. For example, the presence of NO and reducing agents, like CO and propene, facilitates the desorption. Also the exhaust gas coming straight from a combustion engine turns out to be useful for the desorption of these adsorber materials. The addition of lanthana increases the resistance of these zeolite materials against SO₂ poisoning, while on the other hand the NO_x adsorption capacity is lowered simultaneously. An amount of lanthana in the range of 20% seems to be a good compromise. While such adsorber material at the beginning shows same SO₂ adsorption, this adsorption saturates by maintaining a quite high NO_x adsorption capacity of e.g. 6,4mg NO per gram zeolite material.

[0032] Another class of materials promising for use as adsorber material in the present invention are heteropolyacids of the general formula H₃NM₁₂O₄₀ · 6H₂O or H₄NM₁₂O₄₀ · nH₂O with M and N standing for some appropriate chemical element(s), e.g. M being tungsten or molybdenum and N being P, Si or Ge, while n is an integer, such as e.g. n = 14, 15, or 24. Figure 4 shows in a plot diagram an adsorption and desorption cycle examined with H₃PW₁₂O₄₀ · 6H₂O as adsorber material and by applying the approach with supply of a wet desorption air stream at room temperature as described with reference to figure 3. In this diagram the time t is plotted on the abscissa, while on the left ordinate the nitrogen oxide concentration of the exhaust gas output from the adsorber 3 and on the right ordinate the temperature T in the adsorber 3 are given. Further, the behaviour of the temperature in the adsorber 3 is represented by a curve T_A, the total nitrogen oxide concentra-

tion in the exhaust gas outputted is represented by a curve K1 drawn with a continuous line, the NO₂ portion thereof is represented by a dashed curve K2, and the NO portion is represented by a dash-dotted curve K3.

[0033] As can be seen from this diagram, a significant NO_x adsorption by co-adsorption of NO and NO₂ begins at a time t_0 at which the adsorber temperature T_A reaches a range from about 80°C to 100°C. The adsorber temperature T_A then increases further up to about 170°C and the NO_x adsorption continues, while gradually decreasing after reaching a maximum according to the increasing saturation of the adsorber material, as seen by the three nitrogen oxide concentration curves K1, K2, K3 going through a local minimum corresponding therewith. After saturation has been reached, one switches to desorption operation at a time t_1 by stopping the supply of exhaust gas into the adsorber 3 and instead injecting therein the wet desorption air stream at room temperature. This results on the one hand in a gradual decrease of the adsorber temperature T_A to a value of about 80°C by the cooling effect of the air stream. The measured concentration of the nitrogen oxide components in the exhaust gas falls abruptly at the beginning, since the supply of motor exhaust gas has been switched to the supply of the air stream containing substantially less nitrogen oxides and the desorption does not react so fast. The latter then starts gradually until reaching a maximum corresponding to the local maxima of the various nitrogen oxide concentration curves K1, K2, K3 at $t \approx 150$ min, whereafter the desorption decreases to zero. A quantitative comparison reveals that practically all of the nitrogen oxide amount of about 38 mg NO_x per gram adsorber material adsorbed in the previous adsorption cycle has been released in the desorption cycle. It should be noted that heteropolyacid structures are completely resistant to SO₂ poisoning.

[0034] It is understood that besides the disclosed embodiments other realizations of the invention are possible. For example, instead of the exhaust gas recirculation shown some other conventional method of converting the nitrogen oxides released from the adsorber 3 after being temporarily stored therein can be provided, such as a succeeding nitrogen oxide catalytic reduction stage.

Claims

1. Exhaust gas purifying system, preferably for a motor vehicle internal combustion engine, comprising
 - a nitrogen oxide adsorber (3) and
 - adsorber operation means for alternately operating the adsorber in adsorption and desorption mode and for passing the exhaust gas of a combustion source through said adsorber at least in adsorption mode, said operation

means including a desorption gas supply unit (6) for supplying a desorption gas (7) to said adsorber during desorption mode, characterized in that

- said desorption gas supply unit (6) includes pressure swing means for accomplishing a pressure swing of the nitrogen oxide partial pressure when switching from adsorption to desorption mode.
2. Exhaust gas purifying system according to claim 1, further characterized in that said pressure swing means comprises means for supplying a watercontaining, wet desorption gas (7).
 3. Exhaust gas purifying system according to claim 1 or 2, further characterized in that said adsorber operation means include means for increasing or for decreasing or for keeping constant the temperature in said nitrogen oxide adsorber (3) during desorption mode.
 4. Exhaust gas purifying system according to one of claims 1 to 3, further characterized by an oxidizing catalytic converter preceding said nitrogen oxide adsorber (3).
 5. Exhaust gas purifying system according to one of claims 1 to 4, further characterized in that said desorption gas supply unit includes means (6a) for supplying an exhaust gas stream not passed through an oxidizing catalytic converter before, and said adsorber operation means include means for increasing the temperature in said adsorber during desorption mode.
 6. Exhaust gas purifying system according to one of claims 1 to 5, further characterized in that the nitrogen oxide adsorber (3) comprises a Na-Y, Ba-Y or a Ba-La(x%)-Y zeolite mate, with $0 < x < 100$, or a heteropolyacid material of the form $H_3NM_{12}O_{40} \cdot 6H_2O$ or $H_4NM_{12}O_{40} \cdot nH_2O$, with $M = W$ or MO , $N = P, Si, \text{ or } Ge$, and n an integer, as adsorber material.
 7. Method for operating an exhaust gas purifying system having a nitrogen oxide adsorber, preferably a system according to one of claims 1 to 6, in which
 - said nitrogen oxide adsorber (3) is alternately operated in adsorption and desorption mode, during adsorption mode the exhaust gas of a

combustion source being passed through said adsorber and during desorption mode a desorption gas (7) being supplied to said adsorber, **characterized in that**

- when switching from adsorption to desorption mode, a pressure swing of the nitrogen oxide partial pressure is made. 5

8. Method according to claim 7, further **characterized in that** 10
the pressure swing is made by supplying a water-containing, wet gas (7) as said desorption gas to said nitrogen oxide adsorber (3).

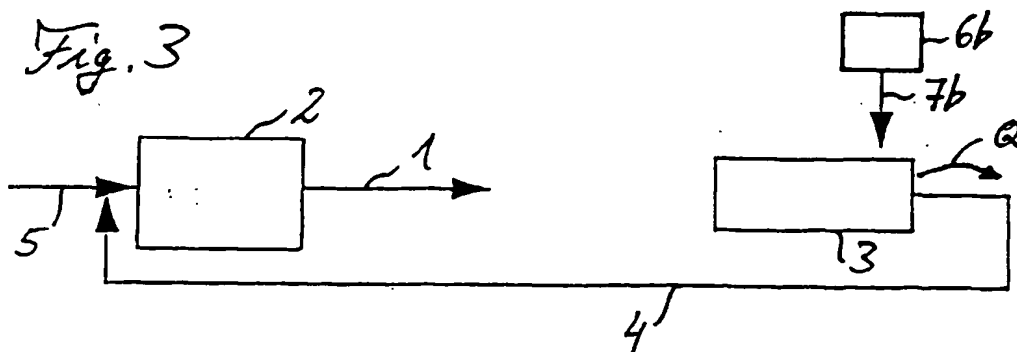
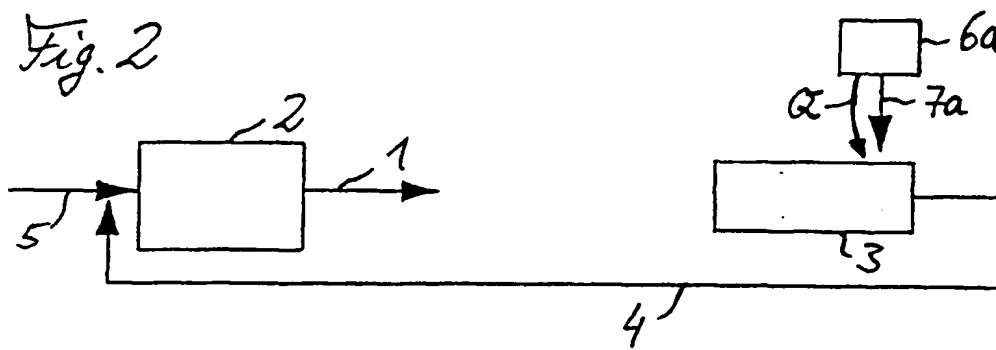
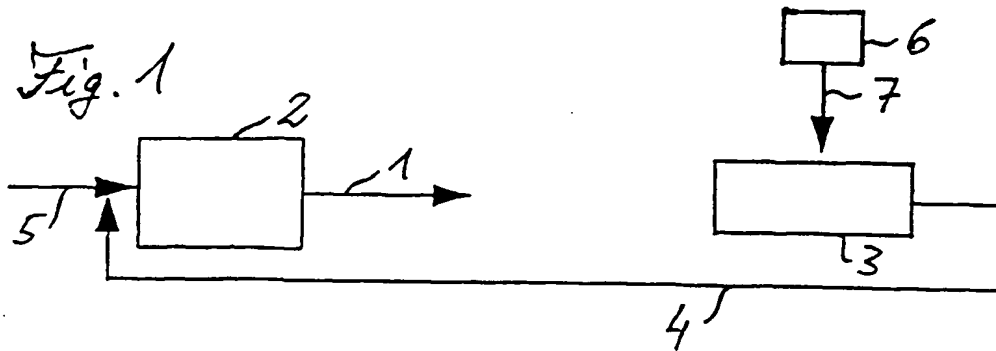
9. Method according to claim 7 or 8, further **characterized in that** 15
the temperature in said nitrogen oxide adsorber (3) is reduced during desorption mode as compared to that in adsorption mode. 20

10. Method according to claim 9, further **characterized in that** 20
the wet desorption gas (7b) is supplied with a temperature lower than the adsorption operation temperature. 25

11. Method according to claim 9 or 10, further **characterized in that**
the temperature during desorption mode is chosen to be lower than 200°C, preferably lower than 100°C. 30

12. Method according to claim 7 or 8 of operating an exhaust gas purifying system having a nitrogen oxide adsorber which includes a Na-Y, a Ba-Y, or a Ba-La(x%)-Y zeolite material, with $0 < x < 100$, or a heteropolyacid material of the form $H_3NM_{12}O_{40} \cdot 6H_2O$ or $H_4NM_{12}O_{40} \cdot nH_2O$, with $M = W$ or No , $N = P$, Si , or Ge , and n an integer, as adsorber material, further **characterized in that** 35
in desorption mode a water-containing, wet gas or an exhaust gas stream not passed through an oxidizing catalytic converter before is supplied to said nitrogen oxide adsorber as said desorption gas to accomplish the pressure swing and the temperature in said adsorber is increased with respect to that in adsorption mode. 40 45 50

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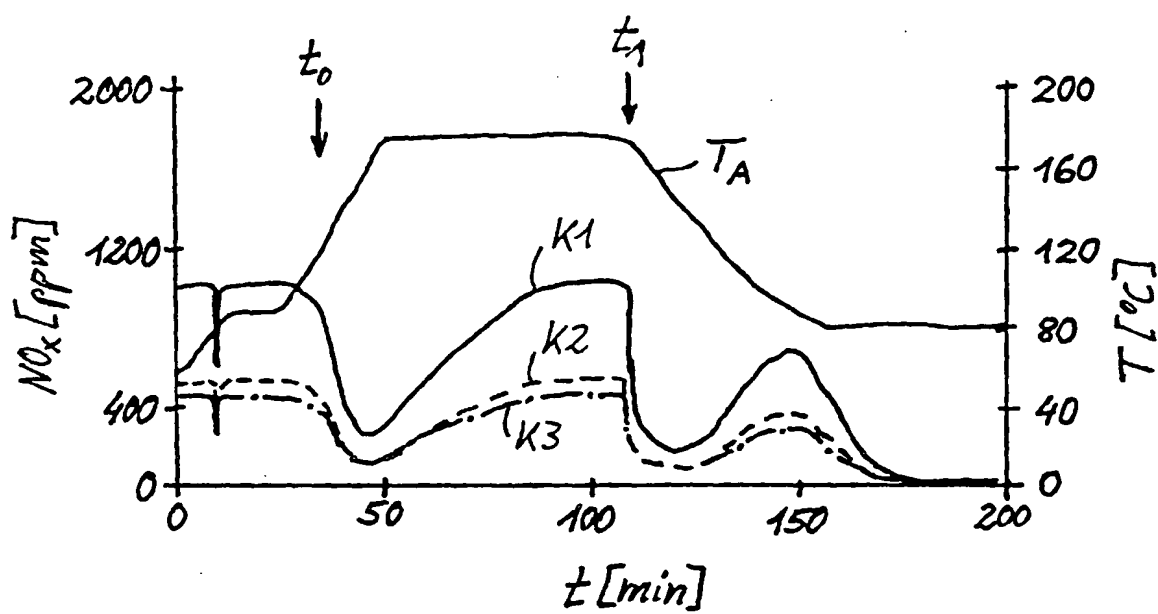


Fig. 4



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 12 3799

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DE 196 28 796 C (DAIMLER-BENZ AG) 23 October 1997 * abstract * * column 3, line 23 - column 7, line 4; figures 1,2 *	1-5,7,8, 12	F01N3/08 F01N3/04
A,D	DE 43 19 294 C (DAIMLER BENZ AG) 19 May 1994 * abstract * * column 2, line 23 - column 4, line 40; figures 1-3 *	1,3-5,7	
A	WO 98 07504 A (VOLKSWAGENWERK AG ;HELD WOLFGANG (DE)) 26 February 1998 * page 7, paragraph 4 - page 9, paragraph 1; figure 1 *	1,7	
A	GB 2 042 365 A (BOC LTD) 24 September 1980		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			F01N
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 May 1999	Examiner Van Zoest, A
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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 12 3799

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17-05-1999

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
DE 19628796	C	23-10-1997	EP	0819462 A	21-01-1998
DE 4319294	C	19-05-1994	DE	59401577 D	27-02-1997
			EP	0628714 A	14-12-1994
			US	5457958 A	17-10-1995
WO 9807504	A	26-02-1998	NONE		
GB 2042365	A	24-09-1980	DE	3007427 A	18-09-1980
			JP	56045724 A	25-04-1981
			ZA	8001054 A	25-11-1981

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82